

KINETICS OF THE REACTION BETWEEN SOLID TEREPHTHALIC ACID AND GASEOUS AMMONIA

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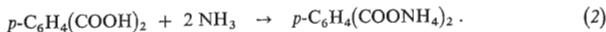
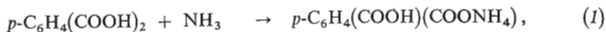
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Received February 16th, 1973

The reaction between solid terephthalic acid and gaseous ammonia was studied in a flow apparatus in the temperature range of 25–240°C. In dependence on the reaction conditions, the reaction product was the monoammonium or the diammonium salt. The reaction course may be described in the kinetic region satisfactorily by the kinetic equation $k^* \tau P_{\text{NH}_3} = 1 - (1 - x)^{1/3}$. Independently of the kinetic measurements, the temperature of the solid phase during the reaction was measured. Temperature changes of the reaction mechanism are discussed.

A process has been developed in our laboratory for purification of terephthalic acid by thermal decomposition of diammonium terephthalate and the following sublimation in a fluid sublimer¹. The evolving gaseous mixture containing terephthalic acid, ammonia and an inert carrier gas enters the condenser, where the separation of terephthalic acid occurs. As it is desirable to obtain a product with a minimum content of ammonia, the terephthalic acid vapours must condense at conditions when the reaction of solid terephthalic acid with gaseous ammonia does not proceed or when this reaction may be neglected. To this purpose, the reaction of solid terephthalic acid with gaseous ammonia was studied at different reaction conditions.

It follows from literature that reactions between solid carboxylic acids and ammonia² are considerably exothermic, the reaction rate is affected favourably by decreased size of solid particles, the reactions proceed easily at room temperature and the reaction product of dicarboxylic acids at different reaction conditions may be the monoammonium or the diammonium salt. Of the parameters which may affect the reaction rate, the following ones were studied in this work: the size of terephthalic acid crystals, partial pressure of ammonia and the reaction temperature. In dependence on the reaction conditions³, monoammonium terephthalate or diammonium terephthalate can be products of the reaction between solid terephthalic acid and ammonia



Formation of the diammonium salt may proceed in one or two stages. Dehydration of the resulting ammonium salts during a following stage can yield at higher temperatures amides and nitriles. These reactions were neglected¹ as their rates were low at the reaction conditions used. The reversed reaction of thermal decomposition of diammonium terephthalate^{4,5} and monoammonium terephthalate was described in the literature. The authors differ in their opinion on the mechanism of thermal decomposition of the diammonium salt. Hájek, Málek and Bažant⁴ have found out that thermal decomposition of the diammonium salt proceeds in one stage, Archipova and Rafíkov⁵ have established that the decomposition proceeds in two subsequent steps with monoammonium terephthalate as an intermediate.

EXPERIMENTAL

Terephthalic acid was prepared by thermal decomposition of diammonium terephthalate and subsequent sublimation in a fluid sublimer at 340–360°C with superheated steam as fluidized gas. The resulting terephthalic acid was purified by further sublimation at the same conditions and screened to fractions of the particle size 0.09–0.2, 0.2–0.315 and 0.315–0.4 mm. The product contained 0.01% ammonia.

Diammonium terephthalate employed for the preparation of terephthalic acid was prepared by saturating an aqueous suspension of terephthalic acid with gaseous ammonia.

Ammonia was a commercial product in pressure cylinders from Chemické Závody SČSP in Krušné Hory.

Apparatus and working procedure. The reaction was studied gravimetrically at atmospheric pressure. A sample of 0.5 g terephthalic acid was poured into a glass basket with the diameter of 15 mm. This basket was suspended on a quartz spiral and placed into a glass tube with the inner diameter of 25 mm and length 300 mm. The gas inlet and thermometer well, which ended approximately 50 mm under the basket, were in the lower part of the tube. The whole tube was placed in an electric furnace with temperature controlled by a variable voltage transformer. Preheating of the gases was secured by a 150 mm-thick layer of steel beads of the diameter of 3 mm in the lower part of the tube. The layer improved the mixing of the gases and simultaneously it decreased the dead volume of the tube. The temperature in the measuring place oscillated in the range $\pm 0.5^\circ\text{C}$. Discharge of ammonium or the ammonium and nitrogen mixture was 100 ml/min in all experiments. Preliminary experiments have confirmed that this velocity of the gas does not affect the experimental accuracy of weight changes. Sensitivity of the quartz spiral was 10 mg/mm and its prolongation was determined by a cathetometer (W. G. Pye, Cambridge, England) with a ± 0.05 mm accuracy. The absolute error in the determination of the conversion of terephthalic acid to its monoammonium or diammonium salt was 1 or 0.5%, resp., for the used amount of terephthalic acid. Besides the kinetic measurements, the temperature of the solid phase was also measured. The same apparatus was used for these measurements with the only exception of a fixed suspension of the basket containing the sample. The temperature of the solid phase was measured with a Fe-constantan thermocouple of the wire diameter of 0.3 mm and with a Cu-constantan thermocouple of the wire diameter of 0.1 mm with their cool ends maintained at 0°C by a mixture of water and ice. The thermocouples were connected to an EZ-3 recorder of Laboratorní přístroje, Prague. At the employed sensitivity of the recorder of 2 mV, the temperature of the solid phase was measured with a $\pm 0.15^\circ\text{C}$ accuracy. Because both thermocouples yielded same results, the error due to heat conduction in the thermocouple

wires may be assumed to be negligible. The temperature measurements at different places of the solid phase during the reaction have proved that the temperature of the solid phase is uniform in the whole volume. Therefore, the hot end of the thermocouple was inserted into the middle of the sample during all measurements.

RESULTS AND DISCUSSION

In initial experiments, the influence was studied of the size of crystals of terephthalic acid on the rate of formation of its ammonium salts. As the surface of the original fractions of terephthalic acid (see the experimental part) was practically identical ($0.2 \text{ m}^2/\text{g}$ by chromatographic measurements) and particles of individual fractions observed microscopically were composed of clusters of terephthalic acid crystals with no simple geometric shape, all fractions were mixed together, ground, and screened to fraction of the crystal size of $0.1-0.125 \text{ mm}$ and $0.2-0.25 \text{ mm}$. The reaction was investigated with these fractions at temperatures of 25 and 200°C and at the partial pressure of ammonia of 1 atm .

In agreement with equilibrium data³, the diammonium salt was identified as the product of the reaction proceeding at 25°C . The volume of the solid phase increased by a factor of three during the experiment and the sample became loose after the reaction. It is clear from Fig. 1 that the reaction rate decreased with increasing the

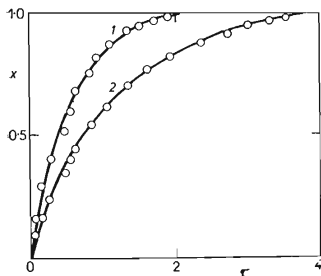


FIG. 1

Dependence of the Degree of Conversion x of Terephthalic Acid to Diammonium Terephthalate on Time τ (h) and the Crystal Size at 25°C

$P_{\text{NH}_3} = 1 \text{ atm}$, 1 $0.1-0.125 \text{ mm}$, 2 0.2 to 0.25 mm .

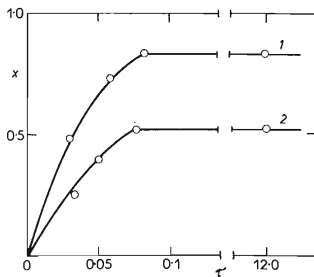


FIG. 2

Dependence of the Degree of Conversion x of Terephthalic Acid to Monoammonium Terephthalate on Time τ (h) and the Crystal Size at 200°C

$P_{\text{NH}_3} = 1 \text{ atm}$, 1 $0.1-0.125 \text{ mm}$, 2 0.2 to 0.25 mm .

crystal size. The product of the reaction proceeding at 200°C was the monoammonium salt. This result also compares well with equilibrium data³. The degree of conversion reached 0.83 after 5 minutes with the crystal size of 0.1–0.125 mm and 0.52 with the crystal size of 0.2–0.25 mm. Then the reaction ceased and no further change could be detected during next 12 hours. The volume of the solid phase remained constant during the experiment and the sample became sintered. The observed dependences are illustrated in Fig. 2. For determining the quality of the reaction products, another experiment was performed at the same reaction conditions with a crystal of the size 10 × 2 × 0.5 mm. The crystal decomposed into thin fibres during the formation of the diammonium salt, for the monoammonium salt it preserved its shape and its surface became sintered.

It follows from these experiments that the reaction starts on the surface of the crystals and the reaction zone then moves into the interior of the solid. The developing layer of the diammonium salt is porous and does not prevent ammonia from coming into contact with the reaction surface. During the formation of the monoammonium salt the reaction surface becomes overheated due to the reaction heat³ (–17.4 kcal/mol). This leads to the formation of the sintered crust which surrounds the crystal and which is entirely impermeable for ammonia.

For the description of solid–gas reactions proceeding by a similar mechanism, the relations deduced from the unreacted-core-shrinking model^{6,7} are often used. It is assumed in this model that the reaction zone advances from the surface into the interior of the particle at the simultaneous formation of an inert permeable layer of products surrounding the unreacted core. The reaction rate may be controlled by the transport of the gaseous component from the bulk volume to the outer surface of the particle, by the transport of the gaseous component through the inert layer of the products towards the reaction surface or by the chemical reaction on the surface of the unreacted nucleus. If we suppose that the reaction is of the zeroth order with respect to the solid component, of the first order with respect to the gaseous component and that the particle is of a spherical shape, the particular processes are described by the following relations^{6,7}: for the rate controlled by the diffusion through the film

$$\tau k_t c_A / R = x, \quad (3)$$

for the rate controlled by the diffusion through the inert layer

$$\tau k_d c_A / R^2 = 1 - 3(1 - x)^{2/3} + 2(1 - x), \quad (4)$$

and for the rate controlled by the chemical reaction

$$\tau k_t c_A / R = 1 - (1 - x)^{1/3}. \quad (5)$$

Time is denoted here as τ , k_f , k_d , k_r are the rate constants of the particular processes, c_A is the bulk concentration of the gaseous component, R radius of the particle and x conversion. The time necessary for reaching the same conversion for particles of different sizes is given by the expressions (for the three cases described by Eqs (3) to (5)):

$$\tau_1/\tau_2 = (R_1/R_2)^{1.5 \sim 2}, \quad (6)$$

$$\tau_1/\tau_2 = (R_1/R_2)^2, \quad (7)$$

$$\tau_1/\tau_2 = R_1/R_2. \quad (8)$$

It is obvious from Fig. 1 that the ratio of the times necessary for reaching the same conversion for crystals of the mean sizes of 0.1125 and 0.225 mm is in the whole range of the experimental dependences equal to 2, i.e. to the ratio of the mean sizes of the crystals. According to relation (8) this means that the chemical reaction is the rate-determining step. In accordance with this, the ratio of the slopes of straight lines obtained by plotting the experimental data in coordinates given by Eq. (5) was equal to 1.96 (Fig. 3). Certain deviations of the experimental points from the straight lines are probably due to the fact that smaller crystals in the fractions are of greater importance for the first stage of the reaction and larger ones for the final reaction stage. The concentration of ammonia in the gaseous phase was expressed by its partial pressure and the resulting value of the rate constant $k' = k_r RT$ was 0.025 mm . atm⁻¹ h⁻¹. By comparing the maximum possible conversions and the corresponding

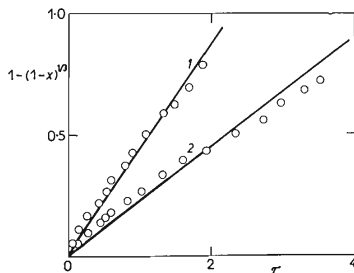


FIG. 3

Experimental Data for the Reaction of the Terephthalic Acid Fractions Yielding Diammonium Terephthalate Plotted in Coordinates of Eq. (5)

$P_{\text{NH}_3} = 1$ atm, $t = 25^\circ\text{C}$, 1 0.1–0.125 mm, 2 0.2–0.25 mm.

times in the case of the formation of the monoammonium salt, the ratio of the slopes of 1.91 was found with the help of Eq. (5), which is in good agreement with the ratio of the mean sizes of the crystals. Thus, the chemical reaction is the rate-determining step till the cessation of the reaction. The value of the rate constant was determined as $k' = 0.3 \text{ mm atm}^{-1} \text{ h}^{-1}$.

The effect of the partial pressure of ammonia on the rate of both reactions was investigated with crystals smaller than 0.1 mm at the partial pressure of ammonia 0.1–1 atm and at 25 or 200°C. For evaluating the magnitude of this effect it was assumed that both reactions were generally of the n -th order with respect to ammonia. For each value of the partial pressure of ammonia, the slope $P_{\text{NH}_3}^n k'/R$ was found with the help of Eq. (5). The values of n were established as slopes of the straight lines in coordinates $\log(P_{\text{NH}_3}^n k'/R)$ and $\log P_{\text{NH}_3}$ (Fig. 4). Both reactions were found to be of the first order with respect to ammonia. The ratio of the rate constants for the formation of the monoammonium (k'_I) and diammonium (k'_{II}) salts from terephthalic acid, $k'_I/k'_{II} = 10.6$, compares well with the ratio of the rate constants obtained from the experiments with crystals of different sizes, $k'_I/k'_{II} = 12$.

It was established from the kinetic measurements performed at different temperatures with crystals smaller than 0.1 mm and at the partial pressure of ammonia of 1 atm that the total reaction rate decreased in the temperature range 25–150°C, the final product was the diammonium salt and the volume of the solid phase increased considerably. At 150–180°C, the reaction rate increases sharply during the initial stage and then the reaction proceeds very slowly yielding the monoammonium salt. The solid phase preserves its shape after the reaction and the product

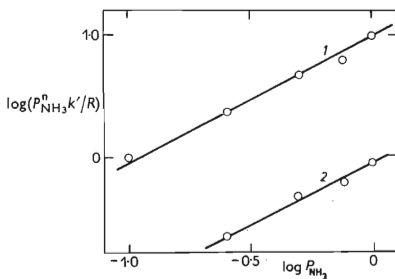


FIG. 4

Determination of the Reaction Order with Respect to Ammonia

1 Monoammonium salt, $t = 200^\circ\text{C}$, 2 diammonium salt, $t = 25^\circ\text{C}$.

becomes partially sintered. At 180–240°C, the reaction rate increases again, the solid phase reacts only to a certain extent and the reaction then ceases to proceed. The product is the monoammonium salt and the samples become entirely sintered. The reaction rate from the beginning till the end is practically independent of temperature. The reaction course at different temperatures is obvious from Fig. 5.

According to equilibrium data³, the sole reaction product at the partial pressure of ammonia of 1 atm and below 187°C should be the diammonium salt and above 187°C the monoammonium one. The formation of the monoammonium salt as a sole product already at temperatures above 150°C suggests that the solid phase is heated above 187°C due to the reaction heat (the reaction of terephthalic acid to the monoammonium salt yields -17.4 kcal/mol and to the diammonium salt -41 kcal/mol)³. To verify this, the temperature of the solid phase was measured during the reaction in dependence on time at different initial temperatures. The experiments were performed on crystals smaller than 0.1 mm at the partial pressure of ammonia of 1 atm. It was found that at 25–180°C the solid phase became overheated by approximately 50°C above the initial temperature and that the time necessary for reaching the corresponding temperature maximum decreased with increasing the initial temperature. This result is in accordance with the fact that the initial reaction rate increases with increasing temperature and that, at 150–180°C, the solid phase is heated sufficiently by the reaction heat evolved to yield the monoammonium salt as the sole reaction product. The temperature of the solid phase during the reaction proceeding at the initial temperature of 25°C decreases rapidly after reaching the temperature maximum at 70°C down to 50°C and then rather slowly to the final temperature equal to 40°C, so that an isothermal course can be postulated for sufficiently long periods of time. This justifies the usage of Eq. (5) for the description of the experimental data. The temperature of the solid phase during the reaction proceeding at the initial temperature above 180°C increases approximately by 70°C.

It was observed during one of the measurements performed at the initial reaction temperature of 25°C that the temperature of the solid phase after reaching its maximum started to oscillate around 40°C with the amplitude of 3°C and frequency $1/3$ min⁻¹. With decreasing the temperature of the solid phase, both the amplitude and the frequency decreased. After closing the ammonia supply, the oscillations ceased and the temperature of the solid phase dropped rapidly to its initial value. This effect may occur during exothermic solid-gas reactions by a combination of subsequent resistances with different temperature dependences (*e.g.* chemical reaction and diffusion)⁸; we were not successful in repeating this experiment.

The decrease in the total reaction rate at 25–150°C may be caused by a temperature dependence of the reaction mechanism. To elucidate this effect, the reaction rate was measured for the formation of the diammonium salt from terephthalic acid and from the monoammonium salt. Both reactions were studied at 25 and 100°C and at the partial pressure of ammonia of 1 atm. Monoammonium terephthalate was prepared

for this purpose in a flow apparatus by the reaction of terephthalic acid and ammonia at 25°C followed by thermal decomposition of the resulting diammonium salt at 200°C and the partial pressure of ammonia of 1 atm. Terephthalic acid was prepared similarly by thermal decomposition of the diammonium salt at 200°C in flowing nitrogen. The volume of the solid phase, which had increased during the formation of the diammonium salt, was preserved after the decomposition in both cases. Both samples were assumed to have identical geometric parameters. Experimental data obtained from the measurements of the reaction rates at 25°C can be described excellently by Eq. (5). The ratio of the rate constants for the formation of the diammonium salt from the monoammonium one (k'_{III}) and of the diammonium salt from terephthalic acid (k'_{II}) was determined as $k'_{III}/k'_{II} = 2.7$. At 100°C, terephthalic acid reacted substantially more quickly than the monoammonium salt and the total reaction rate of both reactions was lower than that at 25°C. The experimental data could not be described by any of Eqs (3)–(5).

It follows from these results that at the initial temperature of the reaction equal to 25°C and the corresponding mean temperature of the solid phase during the measurements of 50°C, terephthalic acid converts into the monoammonium salt with a lower rate than the monoammonium salt into the diammonium one. The total reaction rate is thus determined by the rate of the formation of the monoammonium salt which reacts quickly to yield the diammonium salt during a subsequent step. Thus, the reaction seems to be proceeding in a single step. The cross-section of a reacting particle is composed of two layers: it is the unreacted nucleus of terephthalic acid surrounded by the layer of the resulting diammonium salt. In

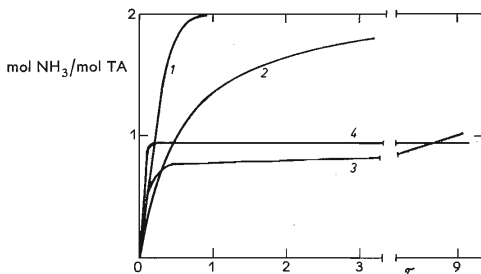


FIG. 5

Time Dependence of the Reaction between Terephthalic Acid Crystals (mol NH_3 per mol of the Acid) Smaller than 0.1 mm and Ammonia at Different Temperatures

$P_{\text{NH}_3} = 1$ atm, 1 25°C, 2 115°C, 3 165°C, 4 200°C.

spite of the fact that the temperature at the reaction interface must be higher than the mean temperature of the solid phase, the equilibrium data³ entitle one to say that the decomposition pressure of ammonia over diammonium terephthalate corresponding to the temperature of the reaction surface will be approximately by two orders lower than the pressure of ammonia over the solid phase and the decomposition pressure over the monoammonium salt will be negligible. We can therefore assume with confidence that the reversed reaction is of no significance and, consequently, the experimental data fit well in Eq. (5). At higher initial temperatures of the reaction, below 150°C, a more complicated mechanism of the overall reaction is to be expected. As at the initial reaction temperature of 100°C the monoammonium salt converts into the diammonium one more slowly than terephthalic acid, the formation of the diammonium salt from terephthalic acid proceeds highly probably in two distinctly separated steps. The reacting particle must be then composed of three layers: the unreacted nucleus of terephthalic acid, a layer of the monoammonium salt and a layer of the diammonium salt. If we further assume that the temperature at the monoammonium-diammonium salt reaction interface is higher than the mean temperature of the solid phase, the decomposition pressure of ammonia over the arising diammonium salt is then comparable with the pressure of ammonia over the solid phase and consequently the reversed reaction appears in a large extent. In accordance with this fact, the rate of formation of the diammonium salt from the monoammonium one decreased with increasing temperature.

It follows from the measurements of the effect of the partial pressure of ammonia on the rate of formation of the monoammonium salt at the initial reaction temperature of 200°C, when the reversed reaction did not proceed even at the partial pressure of ammonia of 0.1 atm (the experimental data could be well described by Eq. (5)), the possible disproportionation of the monoammonium salt at the terephthalic acid-monoammonium salt reaction interface may be neglected and the decrease in the reaction rate with increase in temperature is probably due to the partial decomposition of the diammonium salt at the monoammonium-diammonium salt reaction interface, which affects unfavourably the contact between ammonia and the surface of terephthalic acid. The total reaction rate at higher temperatures is probably controlled by heat removal from the solid phase.

The results of the kinetic measurements performed at the initial reaction temperature of 25°C, when the reaction product is the diammonium salt and the reaction proceeds practically in one step, may be compared with the results of Hájek, Málek and Bažant⁴ who had studied the thermal decomposition of diammonium terephthalate in a fluid layer at the flow rate of the inert gas of 300 l/h and found that this reaction proceeded in one step, too. The pressure of ammonia over the solid phase was negligible in this case and consequently no formation of the monoammonium salt was observed. Both their and our experiments were performed at conditions far from equilibrium. The results of the kinetic measurements made at the initial reaction

temperature below 150°C, where the reaction proceeds in two steps, may be compared with those of Archipova and Raříkov⁵ who found that thermal decomposition of diammonium terephthalate proceeded in two subsequent steps. As they used low flow rates of the inert gas (1.8 l/h), it is possible to assume that the ammonia pressure over the solid phase was not negligible and the thermal decomposition proceeded near equilibrium conditions which probably resulted in partial formation of the monoammonium salt. In our experiments, the decomposition pressure of ammonia over the resulting diammonium salt was comparable with the ammonia pressure over the solid phase, the reaction proceeded near equilibrium conditions, and partial disproportionation of the resulting diammonium salt occurred.

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Translated by K. Hlavatý.